

# AN INTRODUCTION TO GAMESS

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# GAMESS

- General Atomic and Molecular Electronic Structure System
- General purpose electronic structure code
- Primary focus is on *ab initio* quantum chemistry calculations
- Also can do
  - Density functional calculations
  - Other semi-empirical calculations (AM1, PM3)
  - QM/MM calculations

# OVERVIEW OF GAMESS

- Types of wavefunctions
  - Hartree-Fock (RHF, ROHF, UHF)
  - CASSCF
  - CI, MRCI
  - Second order perturbation theory
    - MP2 (closed shells)
    - ROMP2 (spin-correct open shells)
    - UMP2 (unrestricted open shells)
    - MCQDPT(CASSCF - MRMP2)
  - Localized orbitals (SCF, MCSCF)

# OVERVIEW OF GAMESS

- **Energy-related properties**
  - Total energy as function of nuclear coordinates (PES): All wavefunction types
  - Analytic energy gradient
    - RHF, ROHF, UHF, MCSCF, CI, MP2
    - ROMP2, UMP2, DFT in progress
  - Analytic hessian
    - RHF, ROHF, TCSCF
    - MCSCF in progress

# OVERVIEW OF GAMESS

- Energy-related properties (cont'd)
  - Numerical hessians from finite differences of analytic gradients
  - Saddle point (TS) search (requires hessian)
  - Minimum energy path=Intrinsic reaction coordinate
    - Several IRC options - GS2 is most effective
    - Requires frequency input, gradients along path
    - Follow reaction path from reactants through TS to products
    - Build reaction path Hamiltonian (RPH)

# OVERVIEW OF GAMESS

- Energy-related properties (cont'd)
  - Dynamic reaction coordinate (DRC)
    - Add kinetic energy to system at any geometry
    - Add photon(s) to any vibrational mode
    - Classical trajectory using QM-derived energies
    - Requires gradients
  - Monte Carlo sampling (not in distributed code)
  - Molecular dynamics (in progress)

# OVERVIEW OF GAMESS

- Other functionalities

- Spin-orbit coupling

- Any spin states, any number of states
    - Full two-electron Breit-Pauli
    - Partial two-electron (P2e)-very efficient, accurate
    - Semi-empirical one-electron  $Z_{\text{eff}}$
    - RESC (in progress)
    - Averaging over vibrational states

- Derivative (vibronic) coupling: planned

# OVERVIEW OF GAMESS

- Other functionalities

- Localized molecular orbitals (LMO)
- Localized charge distributions (LCD)
- Spin densities at nucleus (ESR)
- NMR spin-spin couplings (in progress)
- NMR chemical shifts (in progress)
- Polarizabilities, hyperpolarizabilities
- IR and Raman intensities





# OVERVIEW OF GAMESS

- QM/MM Methods

- Effective fragment potential (EFP) method for

- Cluster studies of liquids
    - Cluster studies of solvent effects
    - Interfaced with continuum methods for study of liquids and solvation in bulk
    - Covalent link for study of enzymes, proteins, materials

- SIMOMM: QM/MM method for surface chemistry

- QM part can be any method in GAMESS
    - MM part from Tinker (Jay Ponder)



# USING GAMESS

- **GAMESS runs on**
  - Any UNIX-based system available in the US
  - Any Linux-based system
  - Any Macintosh
  - Windows-based PC\_GAMESS available (written by Alex Granovsky, distributed by ISU group)
- **GAMESS can be obtained from**
  - [www.msg.ameslab.gov](http://www.msg.ameslab.gov)
  - License required - no cost

# USING GAMESS

- For Macintosh - drop input file on icon
- For UNIX/LINUX systems requires script
- Output appears in .log file
- Vectors, coordinates, hessians appear in .dat file
- IRC data, numerical restart data for frequencies appear in .irc file

# USING GAMESS

- Input files are modular, arranged in \$groups
- Most common input groups
  - \$SYSTEM: specifies memory, time limit
  - \$CONTRL: specifies basics of calculation
  - \$BASIS: specifies basis set if standard
  - \$DATA: specifies nuclear coordinates, basis set if non-standard
- Other important groups:
  - \$GUESS, \$HESS, \$VEC, \$IRC, \$VIB

## USING GAMESS

- \$ sign specifying group must be in column 2
- All groups must terminate with \$END (this \$ can be anywhere except column 1)

# USING GAMESS

- **\$SYSTEM** group:
  - TIMLIM=(default=600 min)
  - MWORDS=(default=1)
  - MEMDDI=
    - Only relevant for parallel run
    - Total required memory (divide by number of processors to get memory requested/node)

# USING GAMESS

- **\$CONTRL** group:
  - ICHARG= (specifies charge on system)
  - MULT= (specifies spin multiplicity)
    - 1 for singlet, 2 for doublet, ...
  - EXETYP=
    - Check: checks input for errors
    - Run: actual run
  - UNITS=
    - angstroms (default)
    - bohr

# USING GAMESS

- **\$CONTRL group:**
  - **Runtyp=** (type of run)
    - Energy (single point energy run)
    - Gradient (energy 1st derivative wrt coordinates)
    - Optimize (optimize geometry)
    - Hessian (energy second derivative, vibrational frequencies, thermodynamic properties):  
generates \$HESS group in .dat file)
    - Sadpoint (saddle point search: requires hessian in \$HESS group)
    - IRC (performs IRC calculation: usually requires \$IRC group, \$HESS group)



# USING GAMESS

- **\$CONTRL** group:
  - **scftyp=** (type of wavefunction)
    - RHF
    - ROHF
    - UHF
    - MCSCF
    - GVB
  - **mplevl=**
    - 0 (no perturbation theory)
    - 2 (MP2: valid for RHF, ROHF, MCSCF, GVB)

# USING GAMESS

- \$BASIS group:
  - GBASIS=
    - STO
    - N21
    - N31
    - TZV...
  - NGAUSS=(# gaussians for STO, N21, N31)
  - NDFUNC=(# sets of d's on heavy atoms)
  - NPFUNC=(# sets of p's on hydrogens)
  - NFFUNC=(# sets of f's on TM's)

# USING GAMESS

- **\$BASIS group:**
  - DIFFSP=(# sets of diffuse sp on heavies)
  - DIFFS=(# diffuse s functions hydrogens)
- **\$DATA group**
  - Title line (will be printed in output)
  - Symmetry group
    - C1
    - CS
    - CNV 2 (C2V), ...
    - Blank line except C1

# USING GAMESS

- **\$DATA group**
  - Symbol Z xcoord ycoord zcoord
    - Symbol = atomic symbol
    - Z = atomic number
    - xcoord,ycoord, zcoord = Cartesian coords
    - Internal coords is another option
  - Repeat this line for each *symmetry unique* atom (see below)
  - Need to specify basis set after each coordinate line if \$BASIS is not present

# USING GAMESS

- **\$DATA group**
  - symmetry unique atoms
    - $\text{H}_2\text{O}$ : O and 1 H
    - $\text{NH}_3$ : N and 1 H
  - saves CPU time (e.g., numerical hessians only displace symmetry unique atoms)
  - Need to follow conventions in GAMESS manual
    - $C_s$ ,  $C_{nh}$ : plane is XY
    - $C_{nv}$ : axis is Z

# USING GAMESS

- **\$GUESS** group
  - Built-in guess works much of the time
  - **GUESS=MOREAD,NORB=xx \$END**
    - Requires \$VEC group (usually from .dat file)
    - NORB=# MO's to be read in
    - Useful when SCF convergence is difficult
    - Necessary for MCSCF, CI

# LET'S DO A FEW EXAMPLES

- To run GAMESS on cluster:
  - Telnet to tumbe
  - Account: cluster
  - Password: Coca Cola
  - Read the READ.ME.gamess file

# FINANCIAL SUPPORT

- Air Force Office of Scientific Research
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